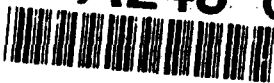


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# A laboratory study of charge transfer and hydrogen atom pickup reactions in $N^+-H_2O(D_2O)$ collisions at suprathreshold energies

James A. Gardner<sup>1</sup>, Rainer A. Dressler, Richard H. Salter and Edmond Murad

*Geophysics Laboratory, GL(AFSC)/PHK, Hanscom AFB, MA 01731, USA*

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Charge transfer and hydrogen atom pickup cross sections are reported for  $N^+-H_2O(D_2O)$  collisions at center-of-mass energies between 1 and 25 eV. Time-of-flight measurements were performed to determine the charge transfer product ion kinetic energies. The exothermic charge transfer proceeds rapidly at large impact parameters with little momentum transfer, and is independent of the water isotope. Above 2 eV, this reaction is governed by a direct mechanism without a long-lived complex. The endothermic hydrogen atom pickup cross section increases with the collision energy, and is approximately two orders of magnitude smaller than the charge transfer cross section.

## 1. Introduction

Gas phase ion-molecule reactions have been extensively studied at near-thermal collision energies both experimentally and theoretically. At these energies, the reaction cross section is governed by both the probability of forming a long-lived collision complex and the phase space available to the products. Phase space theory has successfully reproduced a large number of reaction rates at near-thermal energies [1-3]. At suprathreshold energies, i.e. at center-of-mass collision energies ( $E_{c.m.}$ ) from 1 to 50 eV, the collision complex lifetime is much shorter than a rotational period of the complex, and is therefore insufficient for reaction energy equilibration. Direct mechanisms dominate these reactions, for which no universal theory exists.

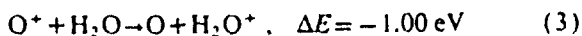
In previous studies of suprathreshold charge transfer collisions, large cross sections have been observed in reactions that proceed efficiently at large impact parameters [4-10]. Little momentum is transferred between the collision partners in these reactions, which exhibit near-resonance between the

reactant and product states. Such behavior has been observed, for example, in the  $N_2^+-H_2O$  [8] and  $N^+-CO_2$  [10] charge transfer systems, which exhibit cross sections of  $(20 \pm 5) \times 10^{-16}$  and  $(7 \pm 2) \times 10^{-16}$  cm<sup>2</sup>, respectively, at  $E_{c.m.} \approx 5$  eV. In those systems, little momentum transfer is observed.

Previously reported [11] cross section measurements for the exothermic [12] ion-water reactions



and



did not include the product ion kinetic energy analysis that is necessary to determine the product ion collection efficiency. The collection efficiency must be known in order to determine integral cross sections from the raw data; the earlier measurements therefore did not represent the integral cross sections for these reactions. The experimental apparatus has since been upgraded [13] to increase the accessible collision energy range and to include time-of-flight measurements that are used for product ion kinetic energy analysis. Integral reaction cross section mea-

<sup>1</sup> Geophysics Research Scholar, 1989-1990.



surements and a product ion kinetic energy analysis have since been reported for reaction (2) [8]. Reaction (3) cross sections have been studied elsewhere in an ICR experiment [7], and those results have been used as a reference for the accuracy of this apparatus and technique [8,13].

We present here detailed results of cross section and time-of-flight measurements for the  $N^+ - H_2O(D_2O)$  charge transfer system over the center-of-mass collision energy range ( $E_{c.m.}$ ) from 1 to 25 eV. The time-of-flight measurements are interpreted to provide the laboratory frame energy of the product ions. This information is utilized to determine the apparatus collection efficiency for the product ions, so that integral cross sections may be reported for reaction (1). Cross sections have also been measured for the endothermic [12] hydrogen (deuterium) atom abstraction channel



and the results are presented here. Extremely low signal levels precluded kinetic energy measurements on the  $ND^+$  products. The raw cross section data are therefore reported as a lower limit to the reaction (4) cross section, and a maximum range is evaluated for this cross section. We have not observed formation of  $NOH^+$  or  $HNO^+$ , although both are possible exothermic products of the reaction (1) collision partners. However,  $NO^+$  has been observed as a product of  $N^+ - H_2O$  collisions, and a detailed study of  $NO^+$  formation will be presented at a later date.

## 2. Experimental and results

The laboratory apparatus consists of a coaxial tandem double mass spectrometer in a high-vacuum system that has been described in detail previously [8,13]. Briefly, an  $N^+$  beam is formed in an electron impact source, then accelerated, mass-analyzed in a Wien velocity filter, and decelerated to the desired experimental collision energy. The ion beam can be pulsed by a set of deflector electrodes to conduct time-of-flight measurements. The primary ion beam passes through a 0.27 cm path-length collision cell, which contains  $H_2O$  at a typical pressure of 0.133 Pa ( $10^{-3}$  Torr). The primary ion beam and the reaction product ions that emerge from the collision

chamber exit aperture are focused onto the entrance of an ELF quadrupole mass filter. The ions are mass-analyzed in the quadrupole, and the selected ions are detected by a channel electron multiplier. The detector output pulses are processed and counted by NIM-module electronics and an AT-compatible computer.

The  $N^+$  beam is formed by electron impact on  $N_2$ . The appearance potential of ground state  $N^+ (^3P)$  from  $N_2$  is 24.32 eV [12]. To assess possible interference from metastable  $N^+ (^1D)$ , which may be formed above 26.2 eV, the charge transfer cross section was measured for several values of the ionizing electron energy. The relative cross sections are shown in fig. 1 for two collision energies. Above the  $N^+ (^1D)$  threshold value, the cross section was observed to rise significantly. Several authors have reported similar effects due to metastable  $N^+$  [14–16]. To minimize the contribution of metastable  $N^+$ , the electron impact source was operated at 26.0 eV electron energy for the remainder of these experiments.

Times-of-flight [8,13] were measured at several collision energies for the  $D_2O^+$  product ions from reaction (1). The product ion energies, listed in table 1, were near-thermal throughout the measured energy range, indicating that there is little momentum transfer from the primary ion to the product ion.

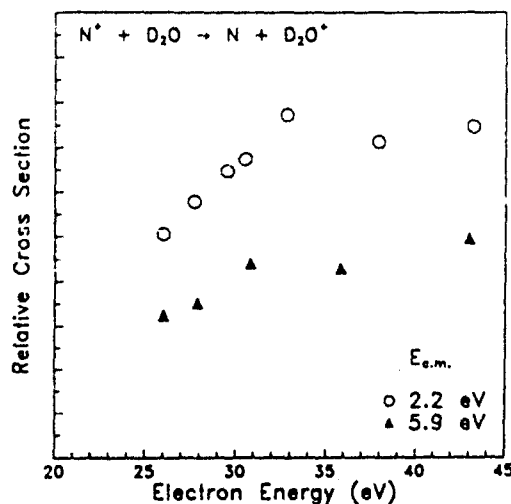


Fig. 1. Reaction (1) relative cross sections as a function of the electron energy at  $E_{c.m.} = 2.2$  eV (open circles) and 5.9 eV (filled triangles).

Table 1  
Primary ion ( $N^+$ ) laboratory energies from retardation potential scans, center-of-mass collision energies, and product ion ( $D_2O^+$ ) laboratory energies from time-of-flight studies for reaction (1)

$E_{lab}(N^+)$ (eV)	$E_{c.m.}$ (eV)	$E_{lab}(D_2O^+)$ (eV)
3.6	2.1	$0.055 (\pm 0.030)$
9.1	5.4	$0.055 (\pm 0.030)$
18.9	11.1	$0.055 (\pm 0.030)$
28.5	16.8	$0.055 (\pm 0.030)$
38.8	22.8	$0.065 (\pm 0.040)$

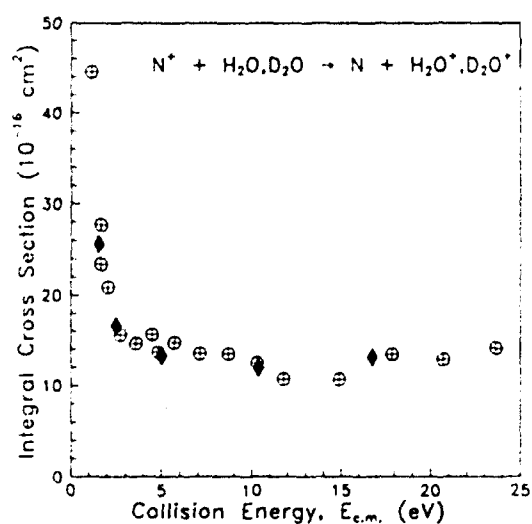


Fig. 2. Reaction (1) integral cross section data as a function of collision energy, with two isotopic forms of water:  $H_2O$  (filled diamonds) and  $D_2O$  (hatched circles).

Integral cross sections are determined by correcting the raw cross section data for the near-thermal ion collection efficiency of the apparatus [9,13]. The integral cross sections for reaction (1) are plotted in fig. 2 as a function of the center-of-mass collision energy. Above  $E_{c.m.} = 2$  eV, the cross section is nearly independent of the collision energy, which is characteristic of a direct mechanism. Below  $E_{c.m.} = 2$  eV, the rapid increase in cross section with decreasing collision energy is indicative of the onset of complex formation, and the cross section values are close to the Langevin limit for this reaction [17–20]. The error in the cross section measurements is estimated to be  $\pm 30\%$ , based on estimates of systematic uncertainties [8]. The cross section does not show an isotope effect.

The observed cross section data for reaction (4) is plotted as a function of the center-of-mass collision energy in fig. 3. Only deuterated water was studied, due to the difficulty in separating  $NH^+$  from the  $N^+$  primary beam in the quadrupole mass spectrometer. The reaction (4) cross section increases moderately with the collision energy, as is typical for endothermic processes above threshold [21]. The combination of the low primary ion beam intensity and a small apparent cross section results in an extremely low  $ND^+$  signal level, producing the relatively large scatter in the fig. 3 data. Due to the low  $ND^+$  signal level, time-of-flight experiments could not be performed, so there is no information regarding the product ion velocity distribution. The apparatus collection efficiency for the  $ND^+$  is therefore unknown, and the observed reaction cross sections must be reported only as lower limits to the true reaction (4) cross sections.

### 3. Discussion

#### 3.1. Charge transfer

The little momentum transfer observed in the reaction (1) charge transfer indicates that near-resonance exists between the reactant and product states.

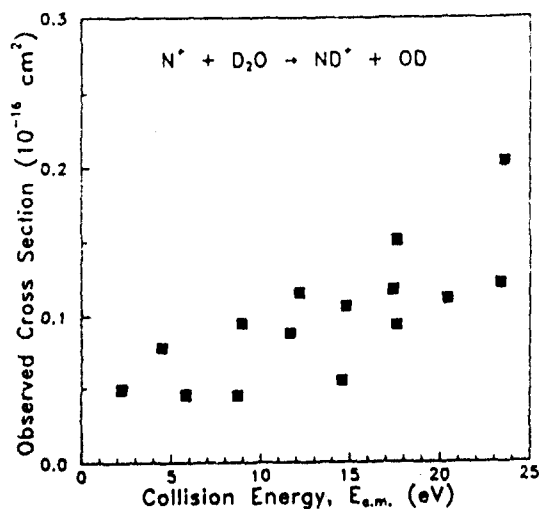


Fig. 3. Reaction (4) observed cross section data as a function of collision energy.

In this reaction, the energy partitioned into internal modes is found to be equal to the reaction exothermicity within the experimental error. It has been postulated [22–25] that the magnitude of the state-to-state cross sections for such a charge transfer process is a function of the Franck–Condon overlap between the reactant and product vibrational wavefunctions. For example, in the case of charge transfer between  $N_2^+$  and  $H_2O$ , energy resonance exists between ground state reactants and the product states in which  $H_2O^+$  is formed in highly vibrationally excited levels ( $\nu_2=14$  or 15) of the  $\tilde{A}^2A_1$  electronically excited state while  $N_2$  is formed in its ground rovibronic state [8,26]. The  $\nu_2$  bending mode is the only  $\tilde{A}$  state vibration that exhibits significant Franck–Condon factors [27]. Recent measurements of  $H_2O^+ \tilde{A} \rightarrow \tilde{X}$  emission have shown that pure bending vibrational levels near-resonance are significantly populated, confirming the applicability of the Franck–Condon overlap principle to that system [26].

In the  $N^+ - H_2O$  charge transfer system, near-resonance exists between ground state reactants and the product states in which  $\tilde{A}$  state  $H_2O^+$  is formed in the  $\nu_2=8$  or 9 vibrational level while ground state  $N(^4S)$  is formed. Recent emission studies [26] have not detected the  $\tilde{A} \rightarrow \tilde{X}$  emissions that would accompany  $H_2O^+$  formation in these levels, even though the  $H_2O^+ \tilde{A}$  state  $\nu_2=8$  and 9 levels exhibit Franck–Condon factors that are greater than those for the levels near-resonance in the  $N_2^+ - H_2O$  case [27]. In reaction (1), the  $H_2O^+$  must therefore be formed in high vibrational levels of the ground electronic state ( $\tilde{X}^2B_1$ ) for which negligible Franck–Condon factors have been observed [27]. Thus, reaction (1) constitutes an example to which the Franck–Condon argument does not apply.

Consideration of electronic orbital angular momentum in the  $N^+ - H_2O$  system may aid in understanding the preference of this system to form  $H_2O^+$  in the  $\tilde{X}$  state rather than in the  $\tilde{A}$  state. A  $P_u$  atomic species (such as ground state  $N^+(^4P)$ ) interacting with a totally symmetric molecular species having  $C_{2v}$  symmetry (such as  $H_2O(^1A_1)$ ) correlates with  $N(^4S)$  and  $H_2O^+(A_2 + B_1 + B_2)$  product states, but not with  $H_2O^+ \tilde{A}$  states [28], assuming that  $C_{2v}$  symmetry is maintained in the collision complex. Thus, if conservation of electronic orbital angular momentum is a major factor in the dynamics of re-

action (1), the reactants would correlate with the  $H_2O^+ \tilde{X}^2B_1$  ground electronic state, but not with the  $H_2O^+ \tilde{A}^2A_1$  state.

### 3.2. Hydrogen atom pickup

Exothermic hydrogen (deuterium) atom pickup reactions (e.g., the formation of  $N_2D^+$  in  $N_2^+ - D_2O$  and  $N_2^+ - D_2$  collisions) have been shown to proceed via a "spectator stripping" type mechanism [8,29]. In such reactions, the product ion is formed with a laboratory velocity slightly below that of the primary ion. The experimental collection efficiency for such strongly forward scattered (laboratory frame) products is essentially 100% in this apparatus. Since reaction (4) is endothermic, the product ions must be formed with laboratory velocities that are significantly lower than those of the primary ion. The necessary translational-to-internal energy transfer can only occur in small impact parameter collisions. The cross section is, therefore, restricted to small values even if the hydrogen atom pickup channel is efficient.

In the absence of time-of-flight data for the product  $ND^+$ , it is not possible to determine the product velocity distribution, which is necessary to report an integral cross section, as mentioned earlier. Although the fig. 3 data are reported as the lower limit to the reaction (4) cross sections, a reasonable range may be evaluated for the actual cross sections. The apparatus minimum collection efficiency is 20.8% for ions that are isotropically scattered in the laboratory frame (i.e. thermal ions) [13]. While the  $ND^+$  products are certainly not isotropically scattered in the laboratory frame, the absolute upper limit to the reaction (4) cross section is obtained by multiplying the ordinates of fig. 3 by a factor of 4.8. It is more likely that the  $ND^+$  velocity distribution will be similar to that of the primary  $N^+$ , so the products would be strongly forward scattered in the laboratory frame. In that case, the product ions would be collected with up to 100% efficiency and the fig. 3 data could represent the integral cross sections for reaction (4). If large angle scattering in the center-of-mass frame is occurring, then the collection efficiency would be reduced to some value below 100%, which in turn would raise the value of the cross section by a currently unknown factor, with the maxi-

imum value of 4.8. In any event, the integral cross section (4) will be less than  $1 \times 10^{-16} \text{ cm}^2$  throughout the investigated energy range. The hydrogen atom pickup channel cross section, therefore, remains more than one order of magnitude smaller than that of the charge transfer channel for the  $\text{N}^+-\text{D}_2\text{O}$  collision system at these energies.

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